Catalytic Applications of Sulfate Grafted Fe_2O_3-ZrO_2 Nanocomposite Oxides for Solvent Free Fine Chemical Synthesis

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This is to certify that the dissertation entitled ***"Catalytic Applications of Sulfate Grafted Fe_2O_3-ZrO_2 Nanocomposite Oxides for Solvent Free Fine Chemical Synthesis"*** *being submitted by* ***Alaka Samal, Lipeeka Rout and Sushree Nibedita Sahu*** *to the Department of Chemistry, National Institute of Technology, Rourkela, Odisha, for the award of the degree of Master of Science in Chemistry is a record of bonafide research work carried out by them under my supervision and guidance. I am satisfied that the dissertation report has reached the standard fulfilling the requirements of the regulations relating to the nature of the degree*.

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Alaka Samal

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Sushree Nibedita Sahu

CHAPTER 1

INTRODUCTION

1.1 General Introduction

Metal oxides are the most extensively studied material having significant electronic, technological and catalytic applications. Metal oxides are used as catalysts or as supports in conjunction with other energetic components for several industrial oxidation, reduction and acid–base catalyzed reaction [1-3]. For example, almost all industrial catalysts contain an oxide as active phase, support or promoter. Metal oxides generally exhibit both electron and proton transfer abilities and can be used as catalysts in redox as well as acid-base reactions. The redox properties of oxides are exploited in catalytic purification systems for complete oxidation of toxic materials [1-5]. The oxide systems with inherent redox properties have also been used for selective oxidation of organic compounds and to synthesize important fine chemicals such as aldehyde, acids and nitriles [2, 3, 7]. The surface acid-base properties of oxides have been taken advantage in carrying out selective organic transformations. Since, the reaction rate on a catalyst surface depends upon the total surface area and the number of active sites present, a good catalyst is required to possess smaller particle and high the surface area. Hence, in the emerging field of nanotechnology, synthesis of oxide nanoparticle have attracted significant interest because of unique physicochemical properties achieved for particles in nanodomain as compared to those of bulk or single particle species [1, 8]. Out of different metal oxides studied in the field of catalysis, zirconia is one of the most extensively studied metal oxides as catalyst or promoter in catalytic processes for several industrial reactions [9-13]. Although ZrO_2 has been used as an acid-base catalyst for numerous organic reactions in heterogeneous catalysis, its application has however been limited by the presence of mild acidic and basic sites on its surface. In this regard

in recent years, there are many investigations on increasing the surface acid strength of zirconia by surface and structural modification [14-18]. The most prominent among them is anchoring catalytically active metal oxides and anions such as WO_3, SO_4^{2-} and MoO_3 at submonolayer level to generate newer acidic sites [14-16]. The results achieved in recent years are quite remarkable considering the fact that strength of the order of 100% H_2SO_4 can be achieved by these modifications which is rarely found in any heterogeneous catalyst. The grafting of sulfated species on ZrO_2 produces strong acidic sites on their surfaces often termed as "superacidic" which are capable of catalyzing carbonium ion reactions under mild conditions. The relatively simple method of preparation of these catalysts makes them one of the attractive classes of heterogeneous catalysts. In addition to the surface treatment, the formation of nanocomposite oxides by doping of suitable metal ions into the zirconia lattice can also generate new active sites. It has been observed that the number of active sites and surface area of sulfated zirconia can be increase by doping transition metal on zirconia and subsequent sulfate grafting or by supporting a small amount of noble metals onto the sulfated zirconia [19, 20].

1.2 Surface and structural modification of zirconia

Although ZrO_2 has been used as an acid-base catalyst for numerous organic reactions in heterogeneous catalysis, its application has however been limited by the presence of mild acidic and basic sites on its surface. In this regard recent years, there are many investigations on increasing the surface acid strength of zirconia by surface as well as structural modification. The most prominent among them is anchoring catalytically active metal oxides and anions such as WO_3, SO_4^{2-} and MoO_3 at submonolayer level to generate newer acidic sites. The results achieved in recent years are quite remarkable considering the fact that strength of the order of 100% H_2SO_4 can be achieved by these modifications which is rarely found in any heterogeneous

catalyst. The grafting of sulfated species on ZrO_2 strong acidic sites on their surfaces often termed as "super acidic" which are capable of catalyzing carbonium ion reactions under mild conditions. The relatively simple method of preparation of these catalysts makes them one of the attractive classes of heterogeneous catalysts. Sulfated metal oxides can be prepared by treatment of the host oxides with sulfuric acids or ammonium sulfate solutions [21]. Acid treatment of the hydrous form of the metal oxides has been reported to produce catalysts with better physicochemical properties. The hydrous form of the metal oxides can be prepared by heat treatment of hydroxide precursors of the metal ions at lower temperature in the range of 300-500^{o}C. The sulfated metal oxides are known to display both Lewis and Bronsted acidic properties. Several surface reaction scheme have been proposed in literature to account for both form of acidity observed in these materials [22, 23].

In addition to the above surface modification by anionic species, the physicochemical properties of sulfate grafted zirconia can be enhanced by incorporation of some transition metal ions into zirconia lattice. It has been observed that the sulfate retention capacity, surface area as well as the number of active sties on the sulfated zirconia can be enhanced by preparing transition metal doped zirconia and subsequent sulfate grafting or by supporting a small amount of noble metals onto the sulfated zirconia [19, 20]. In this regard, zirconia based composite oxides are recently used in place of pure zirconia for preparation of sulfated nanocomposite oxides. Gao *et al*. have reported that the presence of small amount of Al_2O_3 in zirconia matrix increases the catalytic activity and stability of the catalyst for n-butane isomerization [19]. Recently, Ahmed has reported the preparation of sulfated-hafnia promoted zirconia material by precipitation method and studied their catalytic activity for n-butane isomerization at 250°C. The presence of hafnia

increases the surface sulfate density which in turn increases the amount and strength of Brönsted acid sites on the catalyst surface [20].

1.3 Combustion Synthesis Method

Combustion synthesis (CS) or self-propagating high-temperature synthesis (SHS) is an effective, low-cost method for production of various industrially useful materials [18, 24, 25]. This field is important for development of new catalysts and nanocarriers with properties better than those for similar traditional materials. This method is described as a quick, straight forward preparation process to produce homogeneous, well crystalline and unagglomerated multicomponent oxide ceramic powders, without the intermediate decomposition and/or calcination step [24, 25]. Solution combustion synthesis (SCS) a modified form of combustion synthesis is a versatile, simple and rapid process, which allows effective synthesis of a variety of nanosize materials [26]. This process involves a self-sustained reaction in homogeneous solution of different oxidizers (e.g., metal nitrates) and fuels (e.g., urea, glycine, hydrazides). Depending on the type of the precursors, as well as on the conditions used, the SCS may occur as either volume or layer-by-layer propagating combustion modes. This process not only yields nanosize oxide materials but also allows uniform (homogeneous) doping of trace amounts impurity ions in a single step. The combustion reaction is usually initiated in a muffle furnace or on a hot plate at low temperature of about 773 K or less; much lower than the phase transition of the target material. In a typical reaction, a homogeneous mixture of water, metal nitrate precursors and fuel are allowed to dehydrate leading to the exothermic decomposition of the fuel. The chemical energy released from the exothermic reaction between the metal nitrate and fuel appears as large amount of heat which is sufficient enough to raise the temperature of the system to higher value (>1600 K) for a short duration of time. As a result of decomposition of the fuel and the nitrate a

sudden evolution of large volume of gas occurs. This makes large particles or agglomerates get disintegrated leading to the formation of materials, which can be easily crushed to obtain fine particles. Employing this method several oxide materials have been prepared especially for catalytic applications.

1. 4 Objectives of the present study

The main objectives of the present study are

- Synthesis of ZrO_2-Fe_2O_3 nanocomposite oxides by some novel versatile techniques such as solution combustion synthesis and urea hydrolysis method.
- Grafting of sulfate ions on to the ZrO_2-Fe_2O_3 nanocomposite oxides surface to enhance the catalytic activity of ZrO_2-Fe_2O_3 material.
- To study the effect of the iron content and nature on the physicochemical properties of the composite oxides.
- Characterization of the synthesized materials by using various experimental techniques such as XRD, IR, SEM, and UV-Vis to obtain complete information on the physicochemical characteristics of synthesized materials.
- To explore the sulfate grafted xFeZr nanocomposite oxide as efficient heterogeneous catalyst towards environmental benign synthesis of some biologically potent molecules.

CHAPTER 2

MATERIALS AND METHODS

2.1 PREPARATION OF CATALYSTS

2.1.1 Preparation of Fe_2O_3 (x mol%)-ZrO_2 catalysts by combustion method

The ZrO_2, Fe_2O_3, and Fe_2O_3-ZrO_2 composite oxides with 10 and 15 mol% of Fe_2O_3 were prepared by combustion method. Zirconium oxynitrate ($ZrO(NO_3)_2.xH_2O$) (S.D. Fine chemicals India Ltd.), Ferric nitrate $Fe(NO_3)_3.9H_2O$ (Merck India Ltd.) were used as oxidizer and carbohydrazide as fuel for the combustion synthesis. In a typical synthesis procedure for the preparation of Fe_2O_3 (15 mo%).ZrO_2 at a reaction stochiometry of F/O =1 using carbohydrazide as fuel, stoichiometric amount of zirconium oxynitrate, ferric nitrate and carbohydrazide fuel were dissolved in minimum amount of water to obtain a redox mixture. The redox mixture was kept in a muffle furnace preheated at 400^oC. The redox mixture was found to get instantaneously ignited releasing a lot of gaseous products. The combustion residue is subsequently cooled, grinded and calcined at 550 ^oC for 2h to obtain Fe_2O_3 (15 mol%)-ZrO_2 catalysts. Using the same procedure, Fe_2O_3-ZrO_2 composite oxides with 0, 10, 15 and 100 mol% of Fe_2O_3 were prepared using carbohydrazide as fuel.

2.1.2 Preparation of sulfate grafted Fe_2O_3 (x mol%) -ZrO_2 catalyst (SO_4^{2-}/xFe-Zr*)*

The sulfate grafted Fe_2O_3 (x mol%)- ZrO_2 (SO_4^{2-} /xFe-Zr and SO_4^{2-} /xFe-Zr-U) material was prepared by suspending 2 g of the xFe-Zr material in 40 ml of 0.5 M sulphuric acid and stirring the aqueous suspension for 24 h. The solid particles were subsequently filtered and washed with 0.05M sulphuric acid (20 ml portions for 3 times) and calcined at 600^oC for 2h to obtain the (SO_4^{2-} /xFe-Zr and SO_4^{2-} /xFe-Zr-U) materials. Using this procedure, SO_4^{2-} /xFe-Zr materials with Fe_2O_3 content of 10 and 15 mol% were prepared.

2.2 CHARACTERIZATION OF CATALYST

The materials synthesized in section 2.1 were characterized by X-Ray diffraction (XRD), Scanning Electron Microscopy-Energy dispersive X-ray Analysis (SEM-EDAX), UV-Visible spectroscopy (UV-Vis), Infra Red Spectroscopy (IR) and TEM analytical techniques.

X-ray diffraction: The X-ray diffraction patterns of the ZrO_2, Fe_2O_3 and SO_4^{2-} /xFe-Zr samples were recorded on a Philips PAN analytical diffractometer using Ni-filtered $CuK_{\alpha 1}$ radiation. The XRD measurements were carried out in the 2θ range of 20-80^o with a scan speed of 2 degrees per minute.

UV-Vis Spectroscopy:UV-Vis Spectra of pure ZrO_2, Fe_2O_3 and SO_4^{2-} /xFe-Zr materials were recorded using barium sulphate as reference compound on a Shimadzu spectrophotometer (UV-2450) in the range of 200-900 nm.

Infrared Spectroscopy: The IR spectra of different Fe_2O_3 and SO_4^{2-} /xFe-Zr catalyst (as KBr pellets) were recorded using a Perkin-Elmer infrared spectrometer with a resolution of 4 cm^{-1}, in the range of 400 cm^{-1} to 4000 cm^{-1}. Nearly 3-4 mg of the sample was mixed thoroughly with 30 mg of oven dried KBr and made into pallets.

2.3 Synthesis of β-enaminones

Typically, a mixture of aniline (1 mmol), β-dicarbonyl compound (1 mmol) and SO_4^{2-}/15 Fe-Zr catalyst (50 mg) was stirred at 50^{o}C under solvent free condition. Progress of the reaction was periodically monitored by TLC using EtOAc/hexane as eluent. After completion of the reaction, 10 ml of ethyl acetate was added to the reaction mixture and centrifuged at 4000 rpm for 15 minutes to separate the catalyst. The final product was recovered by evaporating the excess solvent and subsequent crystallization from ethanol to obtain pure corresponding enaminones.

CHAPTER 3

Results and Discussion

3.1 XRD study

Figure 3.1 shows the XRD patterns of the pure zirconia, iron oxide and SO_4^{2-}/xFeZr (x= 10, 15%) materials prepared by using carbohydrazide as fuel.

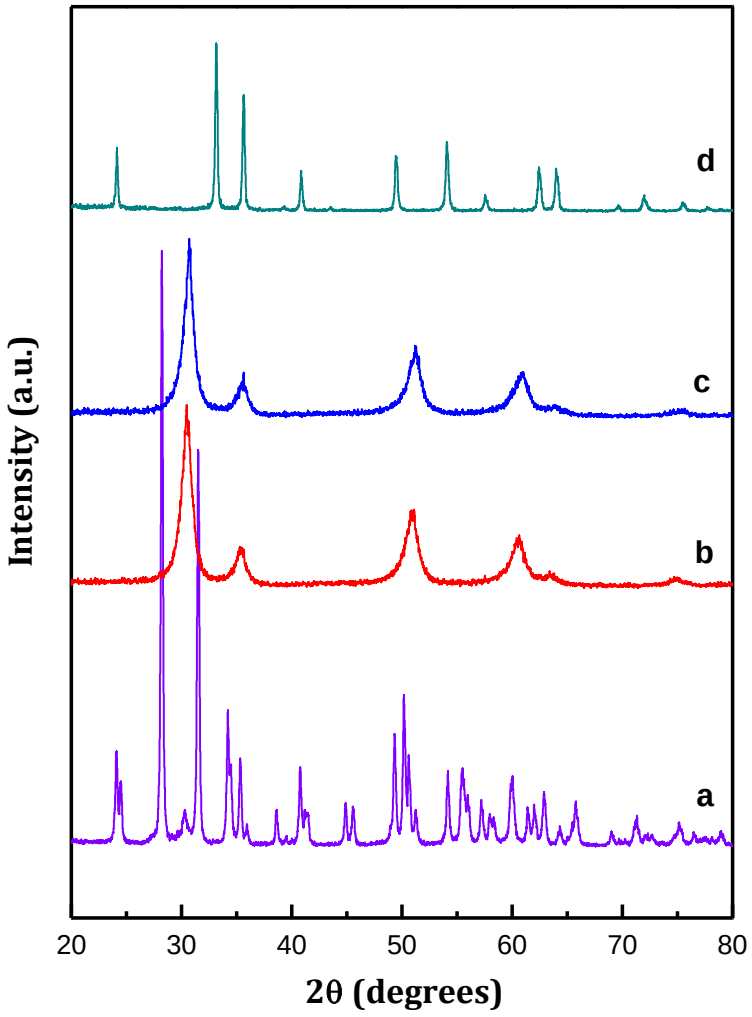


Fig. 3. 1 XRD patterns of combustion synthesized (a) ZrO_2, (b) SO_4^{2-}/10FeZr, (c) SO_4^{2-}/15FeZr and (d) Fe_2O_3

The pure zirconia shows XRD patterns with 2θ values at 28.2 and 31.44 degrees. These peaks correspond to the presence of the monoclinic phase of zirconia. In addition, zirconia shows some

minor reflections corresponding to tetragonal phase of zirconia at 2θ value of 30.2^0 [18, 25]. Addition of iron on to zirconia lattice imparts a significant influence on the zirconia crystal structure. Addition of 10 mol% of iron completely transforms monoclinic to tetragonal phase of zirconia. Essentially, the iron doped sulfate grafted zirconia materials show reflections corresponding to the presence of tetragonal phase of zirconia only. No diffraction peaks corresponding to the presence of crystalline Fe_2O_3 species is observed upto 15 mol% iron oxide content in the composite oxide. This is a clear indication of the presence of well dispersed iron oxide species in the zirconia matrix. The pure Fe_2O_3 oxide shows diffraction peaks at 2θ values of 24.2, 33.1, 35.7, 40.9, 49.4, and 54.1 degrees corresponding to the presence of rhombohedral structure of the α-Fe_2O_3 (hematite) phase [27]. The selective stabilization of the tetragonal phase of zirconia depends on several factors like critical crystallite size, and the presence of phase stabilizer either in the bulk or at the surface. The tetragonal phase of zirconia is also stabilized in presence of aliovalent impurity ions in zirconia lattice [1, 28]. In the present study, stabilization of the tetragonal phase of zirconia can be attributed to the existence of aliovalent dopants such as Fe^{3+} ions in the zirconia lattice which induces oxygen ion vacancy in the crystal lattice of zirconia which in turn helps in the stabilization of the tetragonal phase.

3.2 UV-Vis study

The UV-Vis spectra of the pure ZrO_2, Fe_2O_3 and SO_4^{2-}/xFeZr (x= 10, 15%) materials with different Fe_2O_3 content prepared by combustion method are presented in Fig. 3.2. The pure ZrO_2 prepared by this method shows a sharp and intense band at 230 nm with an absorption edge around 270 nm. ZrO_2 is a direct band gap insulator which shows interband transition in the UV region of the spectrum. The monoclinic form ZrO_2 has two direct interband transitions at 5.93 eV

and 5.17 eV, whereas the tetragonal form has a band gap of 5.1 eV [29]. In the present case the peak a 230 nm can be assigned to the $O^{2-} \rightarrow Zr^{4+}$ charge transfer transition from the monoclinic phase of zirconia which is corroborating to XRD analysis of zirconia. The pure iron oxide shows absorption maxima at 355 nm and 520 nm. The presence of Fe_2O_3 in the zirconia matrix significantly modifies the UV absorption feature of the zirconium dioxide. The xFeZr materials with Fe_2O_3 content (10 and 15 mol%) shows a prominent band at 295 nm along with a broad band at 485 nm. Iron in Fe^{3+} state is expected to show two ligand to metal charge transfer transitions corresponding to the $t_1 \rightarrow t_2$ and $t_1 \rightarrow e$ transitions [30, 31].

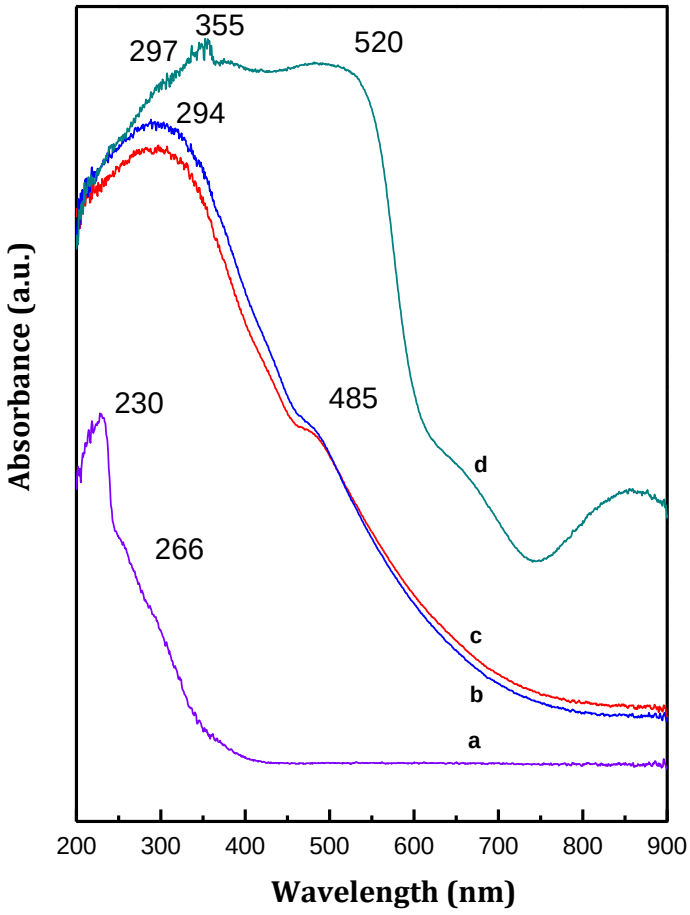


Fig. 3. 2 UV-Vis spectra of (a) ZrO_2, (b) SO_4^{2-}/10FeZr, (c) SO_4^{2-}/15FeZr and (d) Fe_2O_3

However, depending upon the coordination environment of the Fe^{3+} species these transitions differ widely in energies and appear in different region of the spectrum. It has also been reported in literature that the Fe^{3+} present in small nonstoichiometric nanooxide clusters of the type Fe_xO_y shows charge transfer transition in the range of 300-400 nm where as bulk type Fe_2O_3 particle shows UV absorption above 450 nm. In the present study, band at 295 nm can be assigned to isolated octahedral Fe^{3+} species anchored to the zirconia surface and the band at 355 nm can be ascribed to small nonstoichiometric nanooxide clusters of the type Fe_xO_y whereas the peak >485 nm can be assigned to the presence of bulk type Fe_2O_3 particles.

3.3 FTIR study

The FT-IR spectra of pure ZrO_2, Fe_2O_3 and sulfate grafted xFe-Zr materials prepared by combustion method (Panel I) in the spectral region of 400-1500 cm^{-1} are presented in Fig. 3.3. Pure zirconia (Panel I) prepared by combustiom method shows IR peaks at 1120, 747, 518, 447 and 417 cm^{-1}. These IR bands corresponds to the various symmetric and antisymetric structural vibration arising out of zirconia in its pristine state. Sahu and Ranga Rao have reported synthesis of zirconia powder by combustion method using carbohydrazide as fuel [35]. They have mentioned that the IR peaks at 740 and 500 cm^{-1} are typical features of Zr–O–Zr asymmetric and Zr–O stretching vibrations respectively [25]. The occurrence of these bands in the present sample indicates the formation of crystalline zirconia phase. The pure iron oxide shows characteristic IR bands at 543 and 464 indicating the presence of α- Fe_2O_3 phase (hematite) [32]. The sulfate grafted Fe-Zr composite oxides exhibit a series of IR bands in the frequency range of 900-1300 cm^{-1} characteristic to the vibrational features of anchored sulfate groups to zirconia surface [33, 34].

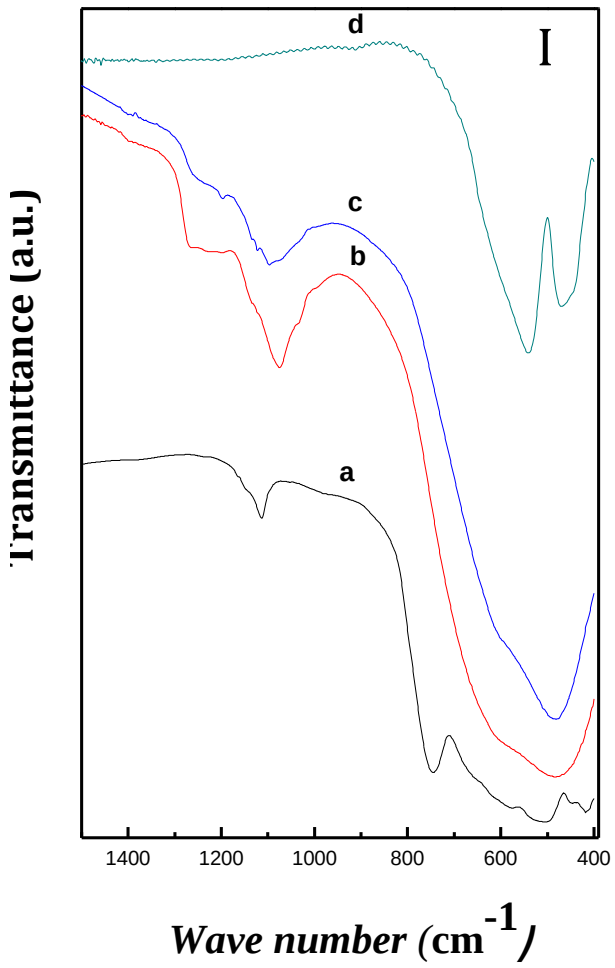


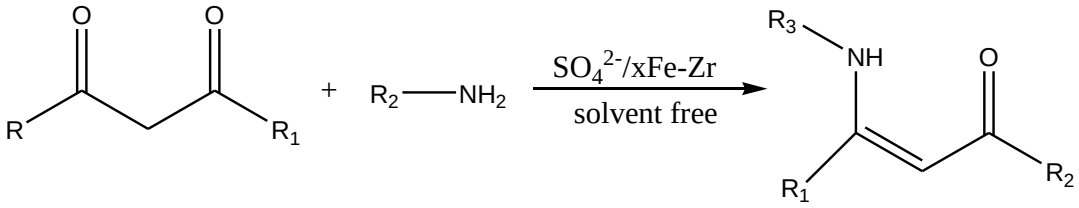
Fig. 3. 5 FTIR spectra of (a) ZrO_2, (b) SO_4^{2-}/10FeZr, (c) SO_4^{2-}/10FeZr and (d) Fe_2O_3

In the present study, a group of spectral bands are observed in the region of 900-1300 cm^{-1}. In the spectral region of 950-1250 cm^{-1}, a series of discrete peaks are observed at 1277, 1240, 1091, 1074 cm^{-1} which are assigned to the various vibrational modes of the S–O bonds of sulfate species connected to the zirconia surface.

3.4 Catalytic activity of combustion synthesized SO_4^{2-}/x Fe-Zr nanocomposite oxide

Enaminones are used as versatile synthetic intermediates for synthesis of a variety of biologically important heterocyclic compounds, nitrogen containing compounds, naturally occurring alkaloids, pharmaceutical drugs with antiepileptic, anticonvulsant, anti-inflammatory and

antitumor properties [35-38]. The traditional method used for the synthesis of enaminones is the direct condensation of an amine with 1,3-diketone in an aromatic solvent with azeotropic removal of water [35]. Recently, some improved procedures have been adopted for enamination of β-dicarbonyl compounds in the presence of various catalysts [36, 37]. In the present investigation, we have evaluated the catalytic activity of SO_4^{2-}/xFe-Zr materials for the synthesis of β-enaminones by condensation of amine and β-dicarbonyl compounds under solvent free conditions (Scheme 1). Initially, the reaction conditions are optimized by taking condensation of aniline and ethyl acetoacetate as model reaction and SO_4^{2-}/xFe-Zr as catalyst at 70°C under solvent free condition [Scheme 1].



Scheme 3.1: Solvent free synthesis of β-enaminones

Among the screened nanocomposite oxide material, the SO_4^{2-}/15 Fe-Zr catalyst display highest catalytic activity. The SO_4^{2-}/15 Fe-Zr catalyst is chosen for further catalytic experiments in the present study. Various reaction parameters such as the catalyst amount, reaction stoichiometry and temperature are varied to obtain the optimized protocol. It is observed that the for a reaction involving 1 mmol of the reactants, 50 mg of the catalyst is ideally suited for efficient condensation of the reactants at 70°C under solvent free condition. After optimizing the protocol, in order to further validate, the versatility of the protocol we have varied aniline by different substituted aniline and ethyl acetoacetate by methyl acetoacetate (Table 3.1).

Table 3.1 Catalytic activity of SO_4^{2-}/15Fe-Zr catalysts

Entry	R	R_1	R_2	Time (h)	Yield (%)
1	C_6H_5	CH_3	C_6H_5	13	88
2	CH_3	OC_2H_5	*o*-ClC_6H_4	2	82
3	CH_3	OC_2H_5	*p*-ClC_6H_4	6	83
4	CH_3	OC_2H_5	*p*-$CH_3OC_6H_4$	7	82

Overall, from this investigation we found that SO_4^{2-}/15 Fe-Zr catalyst is quite effective for synthesis of a variety of β-enaminones under environmentally benign condition. This catalyst is found to be superior as compared to protocols reported earlier in terms of short reaction time, green reaction media, solvent free condition, high yield and recyclable heterogeneous catalyst.

CHAPTER 4

CONCLUSION

The combustion synthesis method has been successfully explored as effective methods for the synthesis of Fe_2O_3-ZrO_2 nanocomposite oxide. The SO_4^{2-}/xFe-Zr nanocomposite oxides are prepared by grafting of sulfate ions on to the surface of composite oxide. XRD study indicates the selective stabilization of the tetragonal phase of zirconia. The presence of sulfate group grafted to the surface of xFe-Zr nanocomposite oxide has been ascertained from FTIR analysis. UV-Vis study indicate the presence of a variety of iron oxide species in the form of isolated, clusters and bulk type particles in the composite oxide. The type of Fe_2O_3 species present in zirconia depends on the amount of iron oxide loading. The SO_4^{2-}/xFe-Zr nanocomposite oxides are highly active for the environmental benign synthesis of β-enaminones under solvent free condition. The synthetic protocols developed in this investigation using surface and structurally modified zirconia materials as catalyst are found to be advantageous in terms of simple experimentation, preclusion of toxic solvents, shorter reaction time, recyclable catalyst with high yield and purity of the synthesized products.

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